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Total wavefunction refinement and charge density analysis of $Z' > 1$ molecular crystals and cocrystal structures: comparison with neutron structural data

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We report for the first time the total constrained refinement of a quantum mechanical wavefunction to X-ray diffraction data.

This means that the geometrical and atomic displacement parameters (ADP's) used to define the structure factors from the wavefunction are completely refined to the X-ray data by a least-squares procedure, using aspherical atomic form factors derived from the quantum mechanical charge density by Hirshfeld atom partitioning [1]. The electronic variables - the orbital coefficients - are refined subject to the restraint/constraint that they minimise the total quantum mechanical energy because there are more parameters than data. Both geometrical refinement and electronic constraints are applied simultaneously, for the first time, using a "block-diagonal" iterative procedure. In addition, refinement/constraint to the structure factor magnitudes is used for the first time. Furthermore, the procedure is extended to remove the previous restriction to $Z'=1$ and single-molecule structures. Each unique molecular wavefunction in the unit cell is self-consistently embedded in the multipole field of its neighbours. The technique is reported using DFT-type wavefunctions in a gaussian basis set expansion.

We report results (geometric parameters and other derived properties) for the dipeptide Gly-L-Ala. Geometrical parameters are compared to those from a neutron diffraction analysis. We also report results for a tripeptide L-Alanyl-L-Tyrosyl-L-Alanine cocrystallizing with dimethylformamide.

[1] D. Jayatilaka, B. Dittrich, *Acta. Cryst. A* **2008**, *64*, 383-393

Keywords: X-ray constrained wavefunction, Hirshfeld atom refinement, charge density analysis

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Topological partition of the crystal elastic constants

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Previous works have demonstrated the partitioning of the bulk modulus and compressibility of solids into contributions due to each atom [1,2] or even to the core, valence, and lone pair electron regions [3,4]. We discuss in this communication how this partitioning, based on Bader's Quantum Theory of Atoms in Molecules, can be extended to the elastic constants, that represent the energy cost of deforming the crystal under small but arbitrary stress forces.

[1] A. Martín Pendás, A. Costales, M.A. Blanco, J.M. Recio, V. Luaña, *Phys. Rev.* **2000**, *B 62*, 13970. [2] T. Ouahrani, A. Otero-de-la-Roza, A.H. Reshak, R. Khenata, H.I. Faraoun, B. Amrani, M. Mebrouki, V. Luaña, *Physica B: Condens. Matter* **2010**, *405*, 3658. [3] J. Contreras-García, A. Martín Pendás, B. Silvi, J. M. Recio, *J. Phys. Chem.* **2009**, *B 113*, 1068. [4] A. Otero-de-la-Roza and V. Luaña, *J. Chem. Theory Comput.* **2010**, *6*, 3761.

Keywords: thermodynamics, calculation, elasticity

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New Gapless Dispersion Surface instead of Usual Erroneous Gappy Dispersion One

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In almost all previous works, the hyperbolic dispersion surfaces of the central proper quadrics have been erroneously derived from reduction of the degree from the bi-quadratic equation that could be defined by the existence of the solutions in the homogeneous simultaneous linear propagation equation with two unknowns as follows:

$$\begin{vmatrix} k_0^2 - k^2 & K^2 C \chi_g \\ K^2 C \chi_g & k_g^2 - k^2 \end{vmatrix} = 0 \quad (1)$$

$$(k_0 + k)(k_g + k)(k_0 - k)(k_g - k) - K^4 C^2 \chi_g^2 = 0 \quad (2)$$

By use of some roughly indefinable approximate relation of $k_0 + k \approx 2K \approx 2k$ and $k_g + k \approx 2K \approx 2k$, the roots of eq. (2) from above factorization of eq. (1) can be given by

$$(k_0 + k)(k_g + k) - 4K^2 = 0 \quad (3a)$$

$$(k_0 - k)(k_g - k) - (K^2 C^2 \chi_g^2 / 4) = 0 \quad (3b)$$

Somehow, the big hyperbola in eq. (3a) has not been adopted but the small one in eq (3b) has been drafted for some reason, which means one of the first serious vandalizations of fundamental eq. (1).

The hyperbola in eq. (3b) could be found in the shape of constricted parts of the cocoon-shaped curve in Fig. 1. Then, by neglecting the high symmetry of eq. (3b) in drawings in Fig. 1, both the branches in eq. (3b) have been substituted by the asymmetric surfaces composed of a pair of a central constricted part of the cocoon-shaped curve and a vertex of the oval in Fig. 1 in imitation of the ellipse without presenting reasonable evidence. This misapplication is the second serious vandalization of it.

Further, very small parts of the Laue circles by dotted lines in Fig. 1 could be substituted as the two tangential lines at L_D , that have been used for the asymptotes of the hyperbola of eq. (3b), also. This is the third serious vandalization of it, without the recognition of the difference between the contact point on the line and its line, which is not curve.

A new original gapless dispersion surfaces could be derived from eq. (1) without crude omission of a term by the usual analogy with the band theory of solid state physics as the closest approximation to the truth. This report including [1] is a part of the extended work of our previous works [2-5].

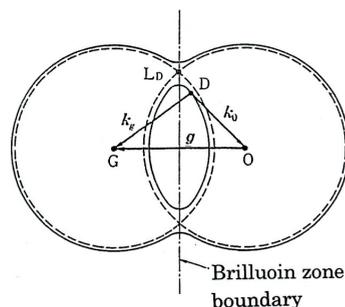


Fig. 1. The conventionally familiar gappy dispersion surfaces.

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Crystal Growth of Friedel's Salt Originated from Pozzolan and Portland Cement

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In the present paper, the Equilibrium Crystal Growth theory is applied to describe Friedel's salt (*Fs*) formation from two different routes C₃A phase of Portland cement (PC) and Al₂O₃^r (reactive alumina) of pozzolans. Both of the reaction courses are contrasted and the role of reactive components (with an emphasis on Al₂O₃^r particularly) is discussed in detail.

The experimental part consisted in PC blends elaboration with different natural and artificial pozzolans, (metakaolin, natural pozzolans, diatomite, silica fume), which were after subjected to chloride attack (3.75% NaCl). For this purpose, two Portland cements of different chemical composition from the C₃A content point of view, have been selected. The samples have been analyzed by XRD and SEM techniques, as well as by selected Cement Chemistry standard methods.

The applied methodology has permitted to opine about the kinetics aspect involved and their direct relation to the physical aspect of the originated crystals. The results show a significant difference in morphology of the Friedel's salt in function of its origin (Figure 1), which is directly related to its formation rate.

The importance of reactive alumina, Al₂O₃^r, component of pozzolans is once again exhibited because of its contribution to the *direct, non-direct*, but above all, *indirect* stimulation of the C₃A phase saline hydration (or non-saline) from the fraction of OPC with which it was mixed, due to its high, fast and early pozzolanic activity and, for this reason precisely, it is found more *specific* than *generic*, intensifying at the same time the Friedel's salt formation from the OPC origin. In contrast, the also high, fast and early pozzolanic activity of reactive silica, SiO₂^r, of pozzolans for the same results is not *specific* at all, on the contrary, it is *unspecific*, or perhaps more precisely, *insufficiently specific* for the same purpose than Al₂O₃^r.

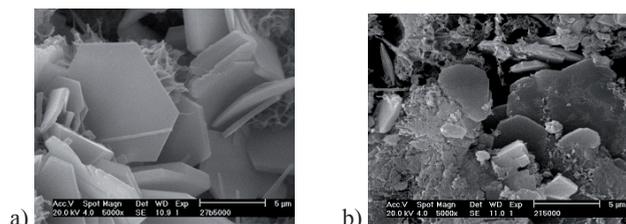


Figure 1, SEM morphology for the Friedel's salt from a) Portland cement and b) pozzolan origin

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Keywords: portland cement, friedel's salt, crystal growth

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FeSe-based superconductors (11, 122-type): phase diagram, crystal growth and characterization

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For over twenty years after discovery by G. Bednorz and K.A. Müller in 1986, complex oxides of copper seemed to be the only compounds showing high temperature superconductivity. This picture of exclusivity was busted by the discovery of superconductivity in MgB₂ (2001) and more recently (2008) in Fe-based compounds. The last discovery was absolutely unexpected as iron spins are usually supposed to be polarized creating magnetic field acting against tendency to build Cooper pairs accountable for superconductivity. Among the iron-based superconductors FeSe has the simplest structure with layers in which Fe cations are tetrahedrally coordinated by Se. The superconducting transition temperature (T_c) was found to be only 8K, but it can be significantly increased (up to 37K) by applying a high pressure or by intercalating potassium into the structure between the FeSe layers [1].

In our recent work [2] we have reported on the discovery of the second member of the family of alkali metal intercalated iron chalcogenides grown by the Bridgman method. This is Cs_{0.8}(FeSe)₂ with T_c around 30K. For the alkali metal intercalated layered compounds known so far, (K_{0.8}(FeSe)₂, Rb_{0.8}(FeSe)₂, Cs_{0.8}(FeSe)₂), the dependence of T_c on the anion height (distance between the layers of Fe and Se) was found to be similar to those reported for As-containing Fe superconductors and Fe(Se_{1-x}Ch_x), where Ch = Te, Se. The steep slope of T_c as a function of anion height suggests that even higher superconducting transition temperatures might be found in the newly discovered FeSe based systems by applying either chemical (substitutional) or hydrostatic pressures.

I will present our recent results of crystal growth and studies of chemical phase diagram and crystal structure of Fe(Se_{1-x}Te_x) and A_y(Fe_{1-x}Se)₂ superconductors (A=K, Rb, Cs) performed by x-ray and neutron diffraction [2-4].

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Keywords: iron, selenide, superconductor